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Quantum scattering via the S -matrix version of the Kohn variational principle

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The S -matrix version of the Kohn variational principle is used to obtain a very effective method for quantum scattering calculations. The approach is especially useful for the nonlocal (i.e., exchange) interactions that arise in chemically reactive scattering (and also in electron-atom/molecule scattering). The particular version developed in this paper has a more general structure than an earlier one by Miller and Jansen op de Haar [J. Chem. Phys. **86**, 6213 (1987)], and applications to an elastic scattering problem, and also to three-dimensional $H + H_2$ reactive scattering, show that it is also more useful in practice.

I. INTRODUCTION

At the most rigorous level of description the theory of chemical reactions is an exercise in quantum mechanical reactive scattering.^{1,2} *Reactive* (or rearrangement) scattering, as contrasted with simpler elastic and inelastic scattering, however, involves nonlocal, exchange-type interactions (if Miller's³ formulation is followed⁴), and this prevents one from being able to integrate the coupled-channel Schrödinger equation by well-established propagation methods⁵ (that *do* work well for elastic or inelastic scattering with local potentials). When dealing with nonlocal interactions it is necessary at some stage to introduce a *basis set* for the scattering coordinate (in addition to the ever-present basis set expansion for all the internal degrees of freedom).

Miller and Jansen op de Haar⁶ recently introduced a basis set method for quantum scattering that has a number of very desirable features: it is exceedingly simple and straightforward, and most importantly it requires that one compute matrix elements only of the Hamiltonian operator itself; i.e., it is not necessary to introduce the Green's function for some reference problem and compute matrix elements involving it (as is necessary in some other approaches^{7,8}). Initial test applications⁶ to elastic, inelastic, and recently to three-dimensional reactive scattering,⁹ showed this method to be quite stable and efficient.

Miller and Jansen op de Haar derived their result using a variational (basis set) approximation¹⁰ to the full scattering Green's function $(E + i\epsilon - H)^{-1} \equiv G^+(E)$, but noted that the equations were identical to those obtained by the S -matrix version of the Kohn variational principle.^{11,12} Previous applications¹³ of the Kohn variational principle had most often used it to calculate the K matrix (or K^{-1}) first, and then obtained an S matrix via the relation

$$S = (1 + iK)(1 - iK)^{-1}, \quad (1.1)$$

which is true for the *exact* S and K matrices. This procedure does *not* produce the same result as applying the Kohn variational approximation directly to the S matrix, however, and in fact this earlier approach is well known¹³ to be plagued by "Kohn anomalies" that have hindered its general usefulness. The S -matrix version of the Kohn variational principle,

though, suffers none of these pathologies; it converges in a well-behaved, nonsingular fashion as the basis set is increased. [To our mind, the superior behavior of the S -matrix version of the Kohn variational principle is related to the fact that the S matrix is a matrix element of the full outgoing wave Green's function $G^+(E)$, while the K matrix is *not*¹⁴ a matrix element of the full standing wave Green's function $PV(E - H)^{-1} \equiv \text{Re } G^+(E)$.] As shown in Sec. II, in fact, the condition that the Kohn approximation to the S matrix be singular gives, identically, the equation for Sigert eigenvalues, which are the physically correct complex poles of the S matrix that characterize scattering resonances. See also the discussion by McCurdy, Rescigno, and Schneider¹⁵ who have adapted the method of Ref. 6 to electron-atom/molecule scattering. [As an aside, we note that these above subtleties do *not* exist for the Schwinger variational principle,¹⁶ another basis set method for scattering. That is, the reader can readily show for himself that use of the Schwinger variational principle with standing wave boundary conditions to obtain K , and then S via Eq. (1.1), gives the identical result to using it with outgoing wave boundary conditions to obtain S directly. Unfortunately, though, the Schwinger variational principle requires that one compute matrix elements involving the Green's function for a reference problem.]

In this paper we utilize the S -matrix version of the Kohn variational principle in a more general way than before^{6,9} and obtain a resulting expression for the S matrix that is preferable to the previous one. The present results are preferable both formally—i.e., they have a more general structure, with no appearance at all of any distorted wave "reference" quantities—and also practically. The practical advantages are that fewer matrix elements are required, and also fewer large sets of simultaneous linear equations need be solved (i.e., fewer multiplications by a large matrix inverse). Section II gives the theoretical development, and applications to elastic and then to reactive scattering are discussed in Sec. III. The elastic tests in Sec. III, e.g., show that the present expression for S converges more rapidly with basis set than others.

II. THEORY

The theoretical development is first carried through for s -wave potential scattering, since this contains all the essen-

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tial ideas. Extension to the general multichannel case is described in Sec. II B.

Also, throughout this paper we adopt the convention that the wave functions in a bra symbol $\langle |$ in bra-ket matrix element notation are *not* complex conjugated. This has seemed to us the least cumbersome way to keep track of the boundary conditions and what is complex conjugated and what is not.

A. Potential scattering

The Hamiltonian is of the standard form

$$H = \frac{-\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r), \quad (2.1)$$

where $V(r) \rightarrow 0$ as $r \rightarrow \infty$. The S -matrix version of the Kohn variational approximation to the S matrix (at energy E) can be written as

$$S = \text{ext} \left[\tilde{S} + \frac{i}{\hbar} \langle \tilde{\psi} | H - E | \tilde{\psi} \rangle \right], \quad (2.2)$$

where $\tilde{\psi}(r)$ is a trial wave function that is regular at $r = 0$ and has asymptotic form (as $r \rightarrow \infty$)

$$\tilde{\psi}(r) \sim -e^{-ikr}v^{-1/2} + e^{ikr}v^{-1/2}\tilde{S}, \quad (2.3)$$

where $v = \hbar k / \mu$ is the asymptotic velocity ($k = \sqrt{2\mu E / \hbar^2}$). “ext” in Eq. (2.2) denotes that the quantity in the square brackets is to be extremized by varying any parameters in $\tilde{\psi}(r)$. For potential (i.e., one-channel) scattering, of course, the S matrix is a 1×1 matrix, a complex number of unit modulus. [As an aside, we note that for a given trial function $\tilde{\psi}$, Eq. (2.2) may also be viewed as the distorted wave Born approximation, where $\tilde{\psi}$ is the distorted wave.]

We take the trial function $\tilde{\psi}(r)$ in the form

$$\tilde{\psi}(r) = -u_0(r) + \sum_{l=1}^N u_l(r)c_l, \quad (2.4)$$

where $u_0(r)$ is a function that is regular at $r = 0$ and has asymptotic form

$$u_0(r) \sim e^{-ikr}v^{-1/2}. \quad (2.5)$$

In applications we have chosen

$$u_0(r) = f(r)e^{-ikr}v^{-1/2}, \quad (2.6)$$

where $f(r)$ is a cutoff function to regularize $u_0(r)$ as $r \rightarrow 0$,

$$\begin{aligned} f(r) &\rightarrow 0, & r &\rightarrow 0, \\ f(r) &\rightarrow 1, & r &\rightarrow \infty; \end{aligned} \quad (2.7)$$

e.g., $f(r) = (1 - e^{-ar})$. The function $u_1(r)$ is

$$u_1(r) = u_0(r)^*, \quad (2.8)$$

and the basis functions $\{u_l(r)\}, l = 2, \dots, N$ are real, square-integrable functions. The coefficients $\{c_l\}, l = 1, \dots, N$ in Eq. (2.4) are the variational parameters in $\tilde{\psi}$. Note that with this form of trial wave function, Eq. (2.4), the quantity \tilde{S} in Eqs. (2.2) and (2.3) is $\tilde{S} = c_1$.

Substituting $\tilde{\psi}$ of Eq. (2.4) into the variational expres-

sion [Eq. (2.2)] gives (after some manipulations)

$$S = \frac{i}{\hbar} \text{ext} \left[\langle u_0 | H - E | u_0 \rangle + \sum_{l,l'=1}^N c_l c_{l'} \langle u_l | H - E | u_{l'} \rangle - 2 \sum_{l=1}^N c_l \langle u_l | H - E | u_0 \rangle \right], \quad (2.9)$$

where the facts have been used that

$$\begin{aligned} \langle u_0 | H - E | u_l \rangle &= \langle u_l | H - E | u_0 \rangle, \\ \langle u_l | H - E | u_{l'} \rangle &= \langle u_{l'} | H - E | u_l \rangle \end{aligned} \quad (2.10a)$$

for $l, l' = 2, \dots, N$, but

$$\langle u_0 | H - E | u_1 \rangle = \langle u_1 | H - E | u_0 \rangle - i\hbar. \quad (2.10b)$$

That is, the transposed matrix elements in Eq. (2.10a) are equal because the surface term that results from integrating by parts twice vanishes [because $u_l(r) \rightarrow 0$ as $r \rightarrow \infty$ for $l \geq 2$], but there is a surface term for the two unbounded basis functions, as given in Eq. (2.10b). As before,⁶ we note that all integrals involving the unbounded basis functions u_0 and u_1 exist because

$$\lim_{r \rightarrow \infty} (H - E) \begin{Bmatrix} u_0(r) \\ u_1(r) \end{Bmatrix} = 0. \quad (2.11)$$

One now extremizes Eq. (2.9) with respect to the expansion coefficients $\{c_l\}$: the equations

$$0 = \frac{\partial}{\partial c_l} [\quad]$$

lead to linear equations for $\{c_l\}$ which are solved by matrix inversion, and the result substituted back into Eq. (2.9). The result of this standard procedure gives the S matrix as

$$S = \frac{i}{\hbar} \left[\langle u_0 | H - E | u_0 \rangle - \sum_{l,l'=1}^N \langle u_l | H - E | u_{l'} \rangle \times (\langle u_l | H - E | u_{l'} \rangle)^{-1} \langle u_{l'} | H - E | u_0 \rangle \right], \quad (2.12a)$$

or in matrix notation

$$S = \frac{i}{\hbar} (M_{0,0} - \mathbf{M}_0^T \mathbf{M}^{-1} \mathbf{M}_0), \quad (2.12b)$$

where

$$M_{0,0} = \langle u_0 | H - E | u_0 \rangle, \quad (2.12c)$$

$$(\mathbf{M}_0)_l = \langle u_l | H - E | u_0 \rangle, \quad (2.12d)$$

$$(\mathbf{M})_{l,l'} = \langle u_l | H - E | u_{l'} \rangle, \quad (2.12e)$$

for $l, l' = 1, \dots, N$ and where “ T ” denotes matrix transpose.

Before discussing Eq. (2.12), we would like to rewrite it in two different ways, one more “elegant” and the other more practical. First, the more elegant version comes from recalling the Löwdin–Feshbach partitioning identity for operators and matrices,

$$(\mathbf{M}^{-1})_{PP} = (\mathbf{M}_{PP} - \mathbf{M}_{PQ} \mathbf{M}_{QQ}^{-1} \mathbf{M}_{QP})^{-1}, \quad (2.13)$$

where P and Q are complementary projectors. If one chooses P to project onto the one basis function $l = 0$, and Q to project onto the $l = 1, \dots, N$ functions, then one can use Eq. (2.13) to write Eq. (2.12b) as

$$S = \frac{i}{\hbar} [(\mathbf{M}^{-1})_{0,0}]^{-1}, \quad (2.14)$$

where here $M_{l,l'} \equiv \langle u_l | H - E | u_{l'} \rangle$ is the matrix in the *total*

space $l = 0, \dots, N$. (Note, though, that $M_{0,1}$ is $\langle u_1 | H - E | u_0 \rangle$, not $\langle u_0 | H - E | u_1 \rangle$.) Equation (2.14) says that one inverts the matrix of $(H - E)$ in the $l = 0, \dots, N$ basis, takes the $(0,0)$ element of this inverse matrix and then inverts it (a 1×1 matrix) to obtain S .

More practically, though, one would like to separate the real part of the inverse matrix calculation from the matrix elements involving both of the energy-dependent complex basis functions u_0 and u_1 . To accomplish this one uses (as before⁶) the following version of the Lödin–Feshbach partitioning identity:

$$(M^{-1})_{QQ} = M_{QQ}^{-1} + M_{QQ}^{-1} M_{QP} (M_{PP} - M_{PQ} M_{QQ}^{-1} M_{QP})^{-1} M_{PQ} M_{QQ}^{-1} \quad (2.15)$$

in Eq. (2.12b), here with Q projecting onto the real functions $l = 2, \dots, N$ and P onto the one function $l = 1$, and this gives

$$S = \frac{i}{\hbar} (B - C^2/D), \quad (2.16a)$$

where

$$B = M_{0,0} - \mathbf{M}_0^T \mathbf{M}^{-1} \mathbf{M}_0, \quad (2.16b)$$

$$D = M_{1,1} - \mathbf{M}_1^T \mathbf{M}^{-1} \mathbf{M}_1, \quad (2.16c)$$

$$C = M_{1,0} - \mathbf{M}_1^T \mathbf{M}^{-1} \mathbf{M}_0, \quad (2.16d)$$

where here the matrix \mathbf{M} and vectors \mathbf{M}_0 and \mathbf{M}_1 are of dimension $l = 2, \dots, N$; i.e.,

$$M_{0,0} = \langle u_0 | H - E | u_0 \rangle, \quad (2.17a)$$

$$M_{1,1} = \langle u_1 | H - E | u_1 \rangle, \quad (2.17b)$$

$$M_{1,0} = \langle u_1 | H - E | u_0 \rangle, \quad (2.17c)$$

$$(\mathbf{M}_0)_l = \langle u_l | H - E | u_0 \rangle, \quad (2.17d)$$

$$(\mathbf{M}_1)_l = \langle u_l | H - E | u_1 \rangle, \quad (2.17e)$$

$$(\mathbf{M})_{l,l'} = \langle u_l | H - E | u_{l'} \rangle \quad (2.17f)$$

for $l, l' = 2, \dots, N$. Equation (2.16) can be further simplified by using the fact that $u_1 = u_0^*$, which leads to the relations

$$M_{1,1} = M_{0,0}^*,$$

$$\mathbf{M}_1 = \mathbf{M}_0^*$$

and thus

$$D = B^*.$$

The final, most compact form of the result is thus

$$S = \frac{i}{\hbar} (B - C^2/B^*), \quad (2.18a)$$

where

$$B = M_{0,0} - \mathbf{M}_0^T \mathbf{M}^{-1} \mathbf{M}_0, \quad (2.18b)$$

$$C = M_{1,0} - \mathbf{M}_0^* \mathbf{M}^{-1} \mathbf{M}_0, \quad (2.18c)$$

$$M_{1,0} = \langle u_0^* | H - E | u_0 \rangle. \quad (2.18d)$$

Equation (2.18) is the final, most useful form of the result (for potential scattering). Maximum use has been made for the symmetry between the incoming and outgoing functions u_0 and $u_1 \equiv u_0^*$ to minimize the number of independent matrix elements which must be calculated; these are $M_{0,0}$, $M_{1,0}$, \mathbf{M}_0 and \mathbf{M} of Eq. (2.17). The matrix inverse in Eq. (2.18) involves only the matrix of $(H - E)$ between the

real, square integrable basis functions. There is no reference in Eq. (2.18) to any distorted wave reference problem as appeared before.⁶ In fact, it was our desire to eliminate this aspect of the previous expression that led to the present development; it seemed unnecessary to us to require the use of a distorted wave representation, since the distorted wave function is not, in general, a good approximation to the true wave function in the interaction region. Use of a plane wave representation is not possible, though, because of repulsive cores in potentials of interest. In the present trial function, Eq. (2.4), the square-integrable function $l \geq 2$ describe the wave function in the interaction region; no functions need be located in classically forbidden (e.g., repulsive core) regions where the true wave function is essentially zero.

We note, though, that it is possible to include distorted wave-like information in the present expression in a very straightforward way if this is desirable (e.g., if there is a long-range, nonreactive interaction, say, that one does not wish to have to describe via the square-integrable basis). One simply chooses the function $u_0(r)$ (and thus $u_1 \equiv u_0^*$) as the (irregular) solution of the distorting potential which has the boundary condition [Eq. (2.5)], multiplied by a cutoff function $f(r)$ to regularize it at $r = 0$. That is, the only rigorous requirement on $u_0(r)$ (and $u_1 \equiv u_0^*$) is that it be regular at $r = 0$ and have the asymptotic form of Eq. (2.5). Choosing it to be the (irregular) solution to the long-range part of the potential would reduce the region that must be spanned by the real square-integrable basis.

Finally, it is useful to emphasize again that Eqs. (2.12), (2.14), and (2.18) (which are all equivalent) have no “Kohn anomalies” that exist in the K -matrix version of the Kohn variational principle.¹³ In fact, the condition that the above expression for the S -matrix be singular—which is most easily deduced from Eq. (2.12)—is

$$0 = \det |\mathbf{M}| \equiv \det [\langle u_l | H - E | u_{l'} \rangle] \quad (2.19)$$

in the space $l, l' = 1, \dots, N$, and one recognizes this as identical to the equation (used by one of us before¹⁷) whose roots are the *Siegert eigenvalues*.¹⁸ These are the physically correct poles of the S matrix at complex energies $E_r - i\Gamma/2$ which characterize the energy and lifetime of scattering resonances. One can also verify explicitly, most easily from Eq. (2.18), that the *real* eigenvalues of the equation

$$\det |\mathbf{M}| = \det [\langle u_l | H - E | u_{l'} \rangle] \quad (2.20)$$

in the space $l, l' = 2, \dots, N$, are *not* poles of the S matrix. If, e.g., E_0 and \mathbf{V}_0 are a real eigenvalue and eigenvector of Eq. (2.20), then Eq. (2.19) for the poles of the S matrix (i.e., the Siegert eigenvalues) can be written as

$$E = E_0 + (\mathbf{M}_1^T \mathbf{V}_0)^2 / M_{1,1}. \quad (2.21)$$

Note that the right-hand side of Eq. (2.21) involves E through the k dependence of the basis function $u_1(r)$. A Golden Rule-like *approximation* to the Siegert eigenvalue can be obtained by choosing $k = \sqrt{2\mu E_0/\hbar^2}$, so that Eq. (2.21) then becomes an explicit (approximate) expression for the complex Siegert eigenvalues.

B. Multichannel (including reactive) scattering

The methodology of Sec. II A generalizes in a straightforward way the case of multichannel scattering. \mathbf{q} denotes the coordinates of the internal degrees of freedom, and $\{\phi_n(\mathbf{q})\}$ the channel eigenfunctions. Trial wave functions $\tilde{\psi}_{n_1}$ and $\tilde{\psi}_{n_2}$ are taken to be the multichannel generalization of Eq. (2.4),

$$\tilde{\psi}_{n_1}(r, \mathbf{q}) = -u_{0n_1}(r)\phi_{n_1}(\mathbf{q}) + \sum_{l=1}^N \sum_n u_{ln}(r)\phi_n(\mathbf{q})c_{ln,n_1}, \quad (2.22a)$$

$$\tilde{\psi}_{n_2}(r, \mathbf{q}) = -u_{0n_2}(r)\phi_{n_2}(\mathbf{q}) + \sum_{l=1}^N \sum_n u_{ln}(r)\phi_n(\mathbf{q})c_{ln,n_2}, \quad (2.22b)$$

where $\{u_{ln}(r)\}$, $l = 2, \dots, N$, is a square-integrable basis set, and $u_{0n}(r)$ [and $u_{1n}(r) \equiv u_{0n}(r)^*$] is the regularized incoming wave for channel n , as in Eqs. (2.5)–(2.7),

$$u_{0n}(r) = f(r)e^{-ik_n r}v_n^{-1/2}, \quad (2.23)$$

where $k_n = \sqrt{2\mu(E - \epsilon_n)}/\hbar$, E being the total energy and ϵ_n the internal energy for channel n . For $l = 0$ and 1, the channel index n includes only open channels, while for $l \geq 2$ the sum over n in Eq. (2.22) includes open and closed channels. For $l \geq 2$ the translational basis functions $\{u_{ln}(r)\}$ need not depend on the channel quantum numbers n , i.e., they may be taken to be the same for all channels. It is possible, though, to use different translational functions for different channels, and this would, in principle, be a more efficient procedure; e.g., closed channels would probably not need as many translational functions as open channels, etc.

The Kohn variations approximation to the S matrix then takes the form (see the Appendix)

$$S_{n_2, n_1} = \text{ext} \left[c_{1n_2, n_1} + \frac{i}{\hbar} \langle \tilde{\psi}_{n_2} | H - E | \tilde{\psi}_{n_1} \rangle \right], \quad (2.24)$$

where ext denotes that the expression in square brackets is to be extremized with respect to the variational parameters in $\tilde{\psi}_{n_2}$ and $\tilde{\psi}_{n_1}$, i.e., $\{c_{ln, n_2}\}$ and $\{c_{ln, n_1}\}$. The variational calculation proceeds essentially the same as in Sec. II A, so we simply give the result of the final, most useful form of the result, analogous to Eq. (2.18):

$$S = \frac{i}{\hbar} (B - C^T B^{-1} C), \quad (2.25a)$$

where B and C (and S) are “small” square matrices $\{B_{n, n'}\}$, $\{C_{n, n'}\}$, $\{S_{n, n'}\}$ in the internal state index n . B and C are given by the appropriate generalization of Eqs. (2.18b) and (2.18c):

$$B = M_{0,0} - M_0^T M^{-1} M_0, \quad (2.25b)$$

$$C = M_{1,0} - M_0^{*T} M^{-1} M_0, \quad (2.25c)$$

where $M_{0,0}$ and $M_{1,0}$ are also small square matrices in the internal state index:

$$(M_{0,0})_{n, n'} = \langle u_{0n} \phi_n | H - E | u_{0n'} \phi_{n'} \rangle, \quad (2.26a)$$

$$(M_{1,0})_{n, n'} = \langle u_{0n}^* \phi_n | H - E | u_{0n'} \phi_{n'} \rangle, \quad (2.26b)$$

M is a “large” square matrix in the composite space of inter-

nal state plus translation,

$$(M)_{ln, l'n'} = \langle u_l \phi_n | H - E | u_{l'} \phi_{n'} \rangle \quad (2.26c)$$

for $l, l' = 2, \dots, N$, and M_0 is a large by small rectangular matrix:

$$(M_0)_{ln, n'} = \langle u_l \phi_n | H - E | u_{0n'} \phi_{n'} \rangle, \quad (2.26d)$$

$l = 1, \dots, N$. Note that the channel quantum numbers n range only over open channels for the small square matrices $M_{0,0}$, $M_{1,0}$, B , C , and S , while it includes both open and closed channels in the large square matrix M . For the large by small rectangular matrix M_0 it includes only open channels in the small direction, and open and closed channels in the large direction.

Equations (2.25) and (2.26) provide a significant advantage over the previous version^{6,9} of the S -matrix Kohn method in that fewer matrix elements are required and fewer sets of simultaneous linear equations must be solved (i.e., multiplications by the inverse matrix M^{-1}). Thus the present version requires two small square matrices, $M_{0,0}$ and $M_{1,0}$ of Eqs. (2.26a) and (2.26b), while the previous one requires three matrices of this type [cf. Eqs. (3.11a), (3.11b), and (3.11c) of Ref. 6]; the present version requires one large by small rectangular matrix, M_0 of Eq. (2.26d), while the previous one requires two such rectangular matrices [cf. Eqs. (3.13a) and (3.13b) of Ref. 6]. As noted in Sec. II A, these economies have resulted because the form of trial wave function has exploited the symmetry of the incoming and outgoing waves. The fact that these matrices are energy dependent, and thus the part of the calculation that must be redone at each different energy E , makes this savings afforded by the present version even more important. Finally, as seen in Eq. (2.25), the present version requires only that one compute the action of M^{-1} on the one rectangular matrix M_0 , i.e., $M^{-1} M_0$, while the previous one requires the action of M^{-1} on the two rectangular matrices that occur in that version [cf. Eq. (3.10) of Ref. 6].

Essentially all of the discussion in Sec. II A following Eq. (2.18) also applies to Eqs. (2.25) and (2.26). For example, the function $u_{0n}(r)$ need not be taken as the (cutoff) free incoming wave as in Eq. (2.23), but can be a distorted incoming wave; it need only be regular at $r = 0$ and have the asymptotic form

$$\lim_{r \rightarrow \infty} u_{0n}(r) = e^{-ik_n r} v_n^{-1/2}. \quad (2.27)$$

For scattering in three-dimensional space, of course, the centrifugal potential is included in the definition of the incoming/outgoing waves, so that the proper asymptotic form is

$$u_{0n}(r) \sim (-ik_n r) h_{l_n}^{(2)}(k_n r) v_n^{-1/2} \sim e^{-i[k_n r - (\pi l_n/2)]} v_n^{-1/2}, \quad (2.28)$$

where l_n is the orbital angular momentum for channel n and $h^{(2)}$ is the spherical Hankel function¹⁹ with the indicated asymptotic form. The simplest choice for $u_{0n}(r)$ [and $u_{1n}(r) \equiv u_{0n}(r)^*$] would thus be the Hankel function in Eq. (2.28) multiplied by a regularizing cutoff function.

Equations (2.25) and (2.26) also apply to reactive (rearrangement) processes by expanding the internal state in-

dex n to incorporate the arrangement index γ ,

$$n \rightarrow n\gamma. \quad (2.29a)$$

The coordinates (\mathbf{q}, r) need also to be labeled by the arrangement index³

$$(\mathbf{q}, r) \rightarrow (\mathbf{q}_\gamma, r_\gamma); \quad (2.29b)$$

$(\mathbf{q}_\gamma, r_\gamma)$ are the Jacobi coordinates for arrangement γ . The matrix elements in Eq. (2.26) between states of different arrangements are the exchange interactions (cf. exchange integrals in electronic structure theory) which are so difficult to treat in the coupled-channel differential equations,³ but which are incorporated in this basis set approach in a rather simple and straightforward manner. The entire calculation thus comes down to choosing basis sets, computing matrix elements of the Hamiltonian, and doing linear algebra.

III. TEST CALCULATIONS

A. Potential scattering

The first test problem is the one used by Stazewska and Truhlar²⁰ to test an approach they have proposed. The Hamiltonian is that of Eq. (2.1) with (in atomic units)

$$V(r) = -e^{-r}, \quad (3.1)$$

and μ the mass of an electron. The real basis is as before,

$$u_l(r) = N_l r^{l-1} e^{-ar}, \quad (3.2)$$

$l = 2, \dots, N$, and

$$\begin{aligned} u_0(r) &= (1 - e^{-ar})e^{-ikr}v^{-1/2}, \\ u_1(r) &= u_0(r)^*. \end{aligned} \quad (3.3)$$

Tables I and II show the fractional error in the tangent of the phase shift for various methods: the Schwinger variational principle (SVP) and the reactance operator variational principal (ROVP), as given in Ref. 20, the previous results of Miller and Jansen op de Haar (MJH),⁶ and the present results of Eq. (2.18). One sees that the present values

TABLE I. Fractional error in $\tan \delta$ as a function of the number of basis functions; $k = 0.15$.^a

$(N-1)^b$	SVP ^c	ROVP ^d	MJH ^e	Present ^f
$\alpha = 2.5$				
2	-1.6463	0.0423	0.4272	0.0277
3	2.2367	0.0003	0.0270	0.0023
4	0.2585	0.0002	0.0024	0.0001
6	0.0164	0.0000	0.0000	0.0000
$\alpha = 1.5$				
2	0.5974	0.0006	0.0006	0.0003
3	0.0565	0.0000	0.0003	0.0000
4	0.0068	0.0000	0.0000	0.0000
6	0.0016	0.0000	0.0000	0.0000

^aFor the potential of Eq. (3.1), the model problem considered in Ref. 20.

^b $N-1$ is the number of real basis functions in the expansion of the trial wave function.

^cResults of the Schwinger variational principle, from Ref. 20.

^dResults of the reactance operator variational principle, from Ref. 20.

^eMiller and Jansen op de Haar, Ref. 6.

^fPresent results of Eq. (2.18).

TABLE II. Fractional error in $\tan \delta$ as a function of the number of basis functions; $k = 0.55$.^a

$(N-1)^b$	SVP ^c	ROVP ^d	MJH ^e	Present ^f
$\alpha = 2.5$				
2	-0.3937	0.0123	-0.0639	-0.0001
3	-0.1236	-0.0384	-0.0104	-0.0019
4	-0.0736	-0.0043	-0.0019	-0.0011
6	-0.0631	-0.0001	-0.0003	-0.0001
$\alpha = 1.5$				
2	-0.0985	-0.0205	-0.0081	-0.0031
3	-0.0888	0.0000	-0.0043	0.0000
4	-0.0649	0.0000	0.0000	0.0000
6	-0.0065	0.0000	0.0000	0.0000

^{a-f}Same as for Table I.

are not only an improvement over the earlier results of Ref. 6, but they are significantly better than the SVP and the ROVP methods, both of which require matrix elements involving a reference Green's function.

A potentially more difficult case to treat is that of a repulsive potential, e.g.,

$$V(r) = +e^{-r}. \quad (3.4)$$

The plane wave version of Ref. 6, e.g., does not work as well in this case²¹ as it does for the attractive potential of Eq. (3.1) (i.e., the MJH results in Tables I and II); this is because the plane wave is nonzero in the classically forbidden region, so that the real basis functions must cancel out the plane wave in that region. Table III shows the results of the present approach, i.e., Eq. (2.18), for the repulsive potential of Eq. (3.4), and one sees that the rate of convergence to the correct result is only slightly slower than for the potential of Eq. (3.1).

In concluding this section we also note that since Eq. (2.18) is a stationary, variational approximation to the *S* matrix, any parameters in the trial wave function—e.g., the nonlinear parameter α in the basis set of Eq. (3.2)—can be

TABLE III. Fractional error in $\tan \delta$ (repulsive potential^a).

$k = 0.15$		
$(N-1)^b$	$\alpha = 2.5$	$\alpha = 1.5$
2	0.0477	0.0030
3	0.0146	0.0002
4	0.0040	0.0000
6	0.0002	0.0000
8	0.0000	0.0000
$k = 0.55$		
$(N-1)^b$	$\alpha = 2.5$	$\alpha = 1.5$
2	0.0241	0.0000
3	0.0054	0.0001
4	0.0006	0.0000
6	0.0000	0.0000

^aFor the potential in Eq. (3.4).

^bSee Table I.

varied to extremize the resulting S matrix. In practice, though, we imagine that it will not prove profitable to vary nonlinear parameters, but rather to take the real basis $\{u_i\}$ sufficiently large that the desired results are insensitive to the precise values of these parameters. Such insensitivity is indeed a (nonrigorous) test to see if the basis is sufficiently large.

B. Reactive scattering

A sample of the three-dimensional reactive scattering calculations of Zhang and Miller⁹ for the $H + H_2$ system were repeated using the present version of the S -matrix Kohn method, as described in Sec. III B. The resulting S -matrix elements were essentially the same as before,⁹ as was the rate of convergence with increasing size of the translational basis and the stability of the results to variations in the cutoff function. In all these respects the two versions of the S -matrix Kohn method behaved essentially equivalently for this example.

The present version of the approach is nevertheless much preferred on several scores. As discussed in the paragraph following Eqs. (2.25) and (2.26), fewer energy-dependent matrix elements must be computed, and fewer sets of simultaneous linear equations must be solved (i.e., actions of the large by large inverse matrix M^{-1}), which must also be carried out anew at each energy. Finally, the fact that the function $u_{0n\gamma}(r_\gamma)$ is given analytically as a function of r_γ , e.g., Eq. (2.28), rather than having a distorted wave elastic scattering function $f_{0n\gamma}(r_\gamma)$ available^{6,9} as numerical values on a grid of r_γ values, means that the exchange integrals involving these functions can be carried out (by numerical quadrature) using mixed coordinate systems that are more efficient than using the translational coordinates r_γ and r_γ themselves. The version of the S -matrix Kohn method presented in this paper is thus clearly preferred for future applications to chemical reactive scattering.

At the request of the referee we give some preliminary information about computation time, though we do not wish to emphasize this because, for one reason, we believe there are several ways that the calculations can be made more efficient. The following computer times refer to the 3D $H + H_2$ reaction ($J = 0$) on the LSTH potential, carried out on the Berkeley Cray X-MP/14, with 36 rotational-vibrational states of H_2 (in each arrangement) and 25 translational functions. Exploiting the symmetry of the three identical particles,³ this leads to large by large matrices of size 900×900 . The energy-independent part of the calculation (primarily numerical integrations to compute the 900×900 matrix of H) requires ~ 3 min, and a little more than 1 min is then required for the calculation at each energy. Of this ~ 16 s is for solution of the simultaneous linear equations to give $M^{-1} \cdot M_0$, with the remainder for the numerical integrations necessary to compute the energy-dependent matrices M_{00} , M_{10} , and M_0 . In order to deal with progressively larger systems it is probably most important to concentrate effort on finding ways to "contract" the basis set, for the $M^{-1} \cdot M_0$ calculation is an N^3 process ($N =$ large dimension) that will ultimately dominate the calculations. Basis set contract is a highly developed art in the quantum chemistry of electronic

structure, and one imagines that many useful ideas from that field can be carried over to the present one.

IV. CONCLUDING REMARKS

By using the S -matrix version of the Kohn variational principle with a more generic type of trial wave functions, Eq. (2.4) (potential scattering) or Eq. (2.22) (multichannel scattering), we have obtained a new more useful basis set approximation for the S matrix. The essential utility of this, and other basis set approaches, is that they apply equally well to the case of nonlocal, exchange interactions as to local potentials.

Equations (2.17) and (2.18) (potential scattering), or Eqs. (2.25) and (2.26) (multichannel scattering), give the basic results. There is no reference to any distorted wave, zeroth problem, though distorted wave-like information can be incorporated into the approach if desired. If the present approach is applied to electron-atom/molecule scattering, for which it should also be quite useful,¹⁵ then one would certainly wish to take the long-range polarization interaction into account this way, i.e., by including this distortion in the definition of $u_0(r)$ [and $u_1(r) \equiv u_0(r)^*$].

The essential practical advantage of the present version of the S -matrix Kohn methods over the previous one^{6,9} is that fewer energy-dependent matrix elements are required and fewer large sets of linear equations must be solved. This substantially reduces the amount of computation that must be done at different energies, a very important consideration in these large calculations.

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APPENDIX: KOHN VARIATIONAL PRINCIPLE FOR THE S MATRIX

Here we give an explicit calculation to show that Eq. (2.24) is indeed a variational (i.e., stationary) expression for the S matrix. The first variation of S_{n_2, n_1} about its exact value is

$$\delta S_{n_2, n_1} = \delta c_{1n_2, n_1} + \frac{i}{\hbar} (\langle \delta \psi_{n_2} | H - E | \psi_{n_1} \rangle + \langle \psi_{n_2} | H - E | \delta \psi_{n_1} \rangle), \quad (A1)$$

where ψ_{n_1} and ψ_{n_2} are the exact solutions of the Schrödinger equation with the boundary conditions contained in Eq. (2.22). Thus,

$$(H - E)\psi_{n_i} = 0, \quad (A2)$$

so that the first term in parentheses in Eq. (A1) is zero.

Integrating with respect to r by parts twice gives

$$\begin{aligned} \langle \psi_{n_2} | H - E | \delta \psi_{n_1} \rangle &= \langle \delta \psi_{n_1} | H - E | \psi_{n_2} \rangle \\ &+ \left(-\frac{\hbar^2}{2\mu} \right) \int d\mathbf{q} \left(\psi_{n_2} \frac{\partial \delta \psi_{n_1}}{\partial r} - \frac{\partial \psi_{n_2}}{\partial r} \delta \psi_{n_1} \right) \bigg|_{r=0}^{r=\infty}. \end{aligned} \quad (\text{A3})$$

Since $(H - E)\psi_{n_2} = 0$ also, only the surface term survives in

Eq. (A3). There is no contribution to it at $r = 0$; as $r \rightarrow \infty$ one has

$$\delta \psi_{n_1}(r, \mathbf{q}) \sim \sum_n \phi_n(\mathbf{q}) u_{1n}(r) \delta c_{1n, n_1}, \quad (\text{A4})$$

$$\begin{aligned} \psi_{n_2}(r, \mathbf{q}) \sim & -u_{0n_2}(r) \phi_{n_2}(\mathbf{q}) \\ & + \sum_n \phi_n(\mathbf{q}) u_{1n}(r) c_{1n, n_2}, \end{aligned} \quad (\text{A5})$$

and inserting Eqs. (A4) and (A5) into Eq. (A3) gives

$$\begin{aligned} \langle \psi_{n_2} | H - E | \delta \psi_{n_1} \rangle &= \left(-\frac{\hbar^2}{2\mu} \right) \lim_{r \rightarrow \infty} \left[-\delta c_{1n_2, n_1} u_{0n_2}(r) u'_{1n_2}(r) + \sum_n u_{1n}(r) u'_{1n}(r) \delta c_{1n, n_1} c_{1n, n_2} + u'_{0n_2}(r) u_{1n_2}(r) \delta c_{1n_2, n_1} \right. \\ &\quad \left. - \sum_n u_{1n}(r) u'_{1n}(r) c_{1n, n_2} \delta c_{1n, n_1} \right] \\ &= \left(-\frac{\hbar^2}{2\mu} \right) \delta c_{1n_2, n_1} \lim_{r \rightarrow \infty} [-u_{0n_2}(r) u'_{1n_2}(r) + u'_{0n_2}(r) u_{1n_2}(r)]. \end{aligned} \quad (\text{A6})$$

One easily finds that the factor in square brackets in Eq. (A6) is $(-2ik_{n_2}/v_{n_2})$, so that using Eq. (A6) in Eq. (A1) gives

$$\begin{aligned} \delta S_{n_2, n_1} &= \delta c_{1n_2, n_1} \\ &+ \left(\frac{i}{\hbar} \right) \left(-\frac{\hbar^2}{2\mu} \right) (-2ik_{n_2}/v_{n_2}) \delta c_{1n_2, n_1} \\ &= \delta c_{1n_2, n_1} + (-1) \delta c_{1n_2, n_1} = 0, \end{aligned} \quad (\text{A7})$$

which proves the variational character of Eq. (2.24).

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